

# A DIVE INTO RUBBER: STRUCTURE - PROPERTY CORRELATION

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## Introduction

Filled and unfilled elastomers are largely employed thanks to their peculiar mechanical behaviour such as their ability to undergo large elastic deformations – that is, to deform and recover their original shape – together with their capacity to dissipate energy. The design and control of their structure and the ability to predict their consequent behaviour in real applications are of paramount importance to fully exploit their potential.

Considering filled polymers, a proper compound's formulation is required for an optimized product performance. Nearly 20 years ago it was reported in literature, "... satisfactory understanding and modelling of the micro-mechanisms by which fillers alter the mechanical behaviour of elastomers has still not been realized" [1]. Motivated by this statement, an extended characterization of different types of compounds, has been carried out during a research activity lasting several years. The compounds have been characterized under different loading conditions from the small strains up to fracture and a correlation between their structural features and the relevant mechanical behaviour has been proposed for the different materials under consideration.

## Results and discussion

Several compounds, differing in the nature of the rubbery matrix (Natural Rubber, Butadiene Rubber, Isoprene Rubber, Styrene-Butadiene Rubber) as well as in the type and content of the filler (carbon black, silica) have been considered.

Different tests were performed on the materials to determine some structural features:

- dynamic-mechanical experiments were carried out under tensile loading conditions to study the effect of filler content on the strain dependence of storage modulus (Payne effect) and to evidence, if present, a "supernetwork" structure in the compound (fig. 1);
- quasi-static uniaxial tensile tests were performed to evaluate stress and strain at break as well the strain at stress upturn in the relevant Mooney-Rivlin plot, related to the maximum chain extension of the rubbery matrix in the compound [4];
- biaxial and pure shear tensile tests have also been performed;
- WAX measurements were performed on stretched specimens to evaluate the strain induced crystallization onset (fig. 2);

- swelling measurements were performed on uncured and cured compounds, the former to estimate the "bound rubber" content and the latter the polymer molecular length between two crosslinks ( $M_c$ );
- DSC measurements were performed to determine the phase structure when polymer blends were used as compound's matrix;
- loading-unloading tests were performed to evaluate the dissipated strain energy and the strain induced softening of the compounds (Mullins effect).

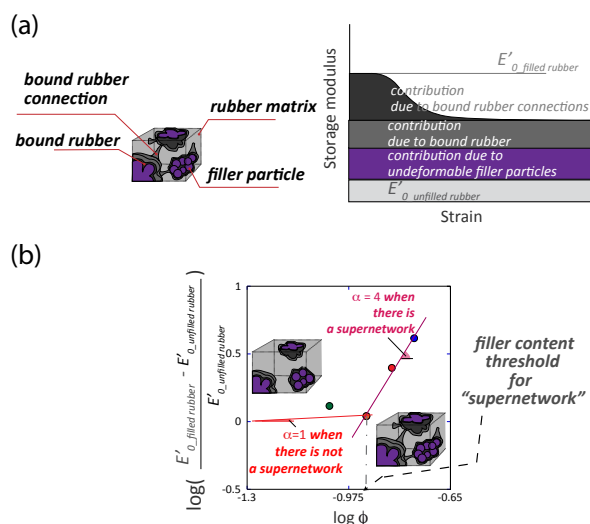


Figure 1: (a) a drawing of a filled rubber structure and of the different contributes to the storage modulus [2]; (b) dependence of the relative increase in the low strain storage modulus ( $E'_0$ ) on filler volume fraction ( $\phi$ ) (data relevant to IR/silica compounds): according to [3] the slope increases from 1 to 4 when a "supernetwork" is formed.

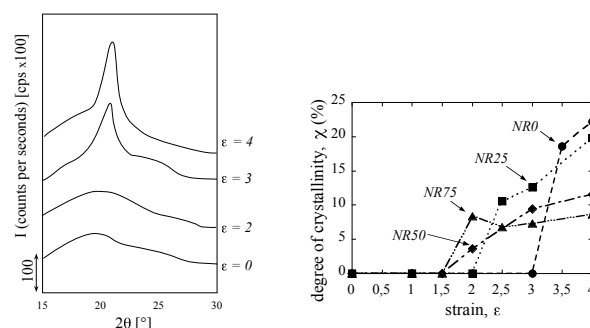


Figure 2: (a) WAX diffraction on a NR based compound filled with 25 phr of Carbon Black N330 at different applied strains, (b) The degree of crystallinity measured is plotted versus the applied strain for different N330/NR compounds to determine the strain at crystallization onset.

Fracture behaviour of the compounds was studied adopting a fracture mechanics approach: notched

specimens were loaded under biaxial and pure shear loading conditions and fracture toughness was measured through stress or energy related parameters. The tests were video-recorded to observe the fracture phenomenology and to perform local deformation measurements using digital image correlation analysis.

It was found that high fracture toughness is observed when the so-called sideways cracks occur (fig. 3).

It was possible to correlate their appearance with polymer orientation and crystallization at the tip of the notch, where larger deformations are localized [5-7].

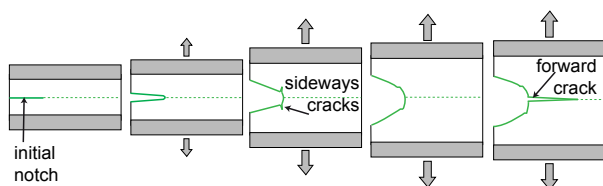


Figure 3: a drawing of the fracture phenomenology observed when sideways cracks form.

These deformation phenomena strengthen the material at the notch tip and high deformations are also reached in the whole specimen at fracture onset: large energy dissipation occurs resulting in high fracture toughness.

Fracture test results will be discussed to highlight how matrix nature, filler type and content, and the presence or not of a “supernetwork” in the compound play a significant role in determining the fracture phenomenology and thus the rubber compound toughness.

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